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PROPERTIES OF EXPLOSIVES

A Study of the Influence of Several Chemical and Thermodynamic Properties
on the Ignition Efficiency of the M1A1 Squib
and the M1A1 Squib Loaded with "Modified" T61 Composition

Project No. TA3-5002, Item G | Report No. 1

Picatinny Arsenal Technical Report No. 1940 | 19 June 1953

Prepared by:

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Chief, Tech Div

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OBJECT

To determine some of the factors which make the M1A1 Squib loaded with "Modified" T61 Composition a more efficient igniter of black powder than the M1A1 Squib, by evaluating several chemical and thermodynamic properties of the charge composition of each squib.

SUMMARY

The mechanism of ignition has been discussed, and related to the several properties of both the M1A1 Squib and the M1A1 Squib loaded with "Modified" T61 Composition. It is shown that the ignition products of the M1A1 Squib loaded with "Modified" T61 Composition attain a much higher temperature than the products of the M1A1 Squib. It is also shown that the heat evolved by the M1A1 Squib loaded with "Modified" T61 Composition is concentrated in a much smaller area, because of the presence of more solid particles. Values for the heat of reaction of each squib charge are calculated and determined experimentally. An analysis of the products of ignition of each squib has been made.

INTRODUCTION:

1. It was reported by the Ammunition Engineering Section that in static firing tests the M1A1 Squib failed to ignite a "Modified" M18 Igniter approximately 4% of the time. The M1A1 Squib was then loaded with "Modified" T61 Composition (and is hereinafter referred to as the "Modified" M1A1 Squib) which gave 100% ignition in the M18 Igniter.

2. To explain the results of the static firing tests it was decided to investigate and calculate several chemical and thermodynamic characteristics of the squib charges which might influence the ignition of the igniter by the squib. The items listed below were determined.

a. Average gas volume per squib
b. Average charge weight per squib
c. Heat of reaction
d. Flame temperature
e. Products of the reaction

3. The compositions of the M1A1 Squib charge and the "Modified" T61 Charge are as follows:

M1A1 Squib Composition		"Modified" T61 Composition	
Diazodinitrophenol	20%	Lead Thiocyanate	36%
Potassium Chlorate	60%	Potassium Chlorate	44%
Carbon (Powdered Wood Charcoal)	15%	Carbon (Powdered Wood Charcoal)	20%
Nitrostarch	5%		

RESULTS:

4. A summary of the results obtained are listed below. The column on the left shows the properties measured and the two columns on the right indicate the results obtained for each squib.

Properties	M1A1 Squib	"Modified" M1A1 Squib
Average Increase in Gas Volume per Squib (cc at 0°C and 760 mm)	12.4 ± .2	8.8 ± .3
Average Charge Weight per Squib (gms)	.0524	.0542
Heat of Reaction, cals/squib (calculated)	71.86	58.03
Heat of Reaction, cals/squib (experimental)	73.13	54.63
Flame Temp, °K (calculated)	1840	3100
Flame Temp, °K (experimental)	1870	2925
*Heat Evolved, per mole of gas (calculated)	25.60	78.62
*Heat Evolved, per mole of gas (experimental)	20.05	74.01
Weight of Solid Products, per squib (gms)	.01986	.03033

*This calculation is based on the actual moles of each gas formed in the reactions of Tables III and IV.

DISCUSSION OF RESULTS:

5. Mechanisms of Ignition:- There are several mechanisms by which the ignition of a powder or explosive has been explained. A substance can be ignited by thermal decomposition of the molecules, tribochemical decomposition of the molecules as by friction or impact, catalysis, supersonic vibrations, static electricity, pressure, and by other methods which are less significant. Ignition can best be explained thermally. Bowden and Yoffe (Ref A) have shown that even the mechanical initiation of a solid or liquid explosive can be explained by the formation of a localized hot spot. It appears that ignition takes place when an adequate amount of energy is evolved to decompose a critical number of molecules. To measure the heat produced, several thermochemical, chemical and physical properties of the M1A1 Squib and the "Modified" M1A1 Squib are measured and compared. All properties such as heat capacity, flame temperature, heat of combustion and heat of formation used in this report are at constant pressure, in order to simulate the actual firing condition of a squib. Because the M1A1 Squib and the "Modified" M1A1 Squib were fired in a closed bomb at constant volume and one atmosphere pressure, the correction for the increase in pressure developed by the gaseous products is included. The properties measured and the method of measuring these properties follow:

6. Properties: -

a. Pressure:

The average increase in gas volume produced by ignition of the "Modified" M1A1 Squib corrected to $0^{o}C$ and 760 mm pressure is $8.8 \pm .3$ ml/squib where .3 ml is the standard deviation of the mean. The average charge weight is .0542 gms per squib. The results are tabulated in Table I. The average increase in gas volume produced by ignition of the M1A1 Squib is $12.4 \pm .2$ ml and the average charge weight is .0524 gms per squib (Table II). This increase in volume is not the actual volume of gases produced by the ignition of the squib. Tables III and IV indicate that the oxygen of the air in the bomb also takes part in the reaction. The increase in volume is used in this report principally to indicate the pressure developed by the products of the squib.

b. Heat of Reaction and Products of Reaction:

The calculated and experimental values for the heat of reaction are shown under Results. The calculated values for flame temperature and heat evolved per mole of gas are based on the calculated heat of reaction. The experimental values for flame temperature and heat evolved per mole of gas are based on the experimental heat of reaction.

To calculate the heat of reaction a knowledge of the products of reaction as well as a knowledge of the heat of formation of each product formed is necessary viz $\sum \Delta H_f$ prod $- \sum \Delta H_f$ reac $= \Delta H_R$ where (ΔH_R)

Discussion of Results (contd)

is the heat of reaction. An analysis of the solid residue of the "Modified" M1A1 Squib after reaction indicates the presence of lead oxide, potassium chloride, and sulfur as well as unreacted carbon. The gases formed in the reaction of each squib charge are shown in Table V. The total products of reaction for each squib are described by the chemical reactions in Tables III and IV. The numerals above each substance indicate the weight in grams of that substance taking part in the reaction. The numerals below the equation represent the equivalent weights. It was assumed that the solid products of the M1A1 Squib consisted entirely of unreacted carbon and potassium chloride. The heat of formation of the products of ignition are shown in Table VI. Details for calculating the heat of reaction are shown in Appendix I.

In Tables III and IV it is noted that carbon dioxide is formed rather than carbon monoxide. This is not unusual in oxygen deficient systems such as exist in the charge composition of each squib. Patai and Hoffman (Ref B), J. Corner (Ref C), Morris and Thomas (Ref D) and others report similar observations. Patai and Hoffman discuss the reaction of carbon and potassium chlorate. J. Corner shows that low temperatures and pressures favor the formation of carbon dioxide. Morris and Thomas show that the products of modern explosives consist almost uniquely of carbon dioxide, water, and nitrogen with the possible formation of carbon monoxide and hydrogen in oxygen deficient systems such as exist in the two squibs studied. Some carbon dioxide is formed by the reaction of the carbon of the squib charge and oxygen of the atmosphere. The latter reaction is shown as the final reaction in Tables III and IV. The extent to which the oxygen of the air will react with a reactant of a squib charge, when this charge is embedded in an igniter, is not known.

The last two reactions for the M1A1 Squib (Table IV) involving the dissociation of water and the oxidation of carbon may be combined. It is doubtful that so large a percentage of water would dissociate at the relatively low flame temperature, which is assumed to be the maximum temperature of the reaction. It is possible however that carbon reacts directly with the water to yield hydrogen. It is also probable that carbon monoxide formed will react with water to give carbon dioxide and hydrogen. This is the water gas reaction, viz $CO + H_2O = CO_2 + H_2$. The overall effect, however, on the heat of reaction and the flame temperature is the same as if the carbon reacted directly with the water.

The heats of formation shown in Table VI are taken from Bichowsky and Rossini (Ref E) with the exception of nitrostarch and diazodinitrophenol.

The heat of formation of diazodinitrophenol is not listed in the literature. It was derived therefore from the heat of combustion of this compound which was determined in these laboratories and is 3.2×10^3 cals/gm. This value should not be taken as absolute however due to the instability of diazodinitrophenol. The chemical reaction for the heat of combustion may be written as $C_6H_2N_4O_5 + 4O_2 \rightarrow 6CO_2\ (g) + H_2O\ (l) + 2N_2$. The heat of formation of diazodinitrophenol ($-\Delta H_f$ diaz) is obtained from the equation:

Discussion of Results (contd)

$6 \Delta H_f\ CO_2 + \Delta H_f\ H_2O - \Delta H_f$ diaz $= -\Delta Hc$ where $(-\Delta Hc)$ is the heat of combustion of diazodinitrophenol. The heat of formation of diazodinitrophenol derived from the above equation is -43 kcal/mole. The negative sign indicates that heat is absorbed.

The heat of formation of nitrostarch is reported by Bertholet (Ref G). Bertholet's formula for nitrostarch is $C_6H_8O_4(HNO_3)$. This indicates a 6.8% nitrogen content as, compared to the 12.75% nitrogen content of the nitrostarch in the M1A1 Squib. It was therefore decided to use the same heat of formation for nitrostarch (12.75% nitrogen content) as for cellulose nitrate (12.66% nitrogen content) which is reported by Jessup and Prosen (Ref H). The heat of combustion for cotton and wood cellulose reported by Jessup and Prosen is 4165.0 and 4172.8 cals/gm respectively. The heat of combustion of potato starch determined by the Picatinny Arsenal Laboratories is 4165.1 cals/gm. It is evident therefore that the heats of combustion of the two compounds are practically identical. Each molecule contains the same number of carbon, oxygen and hydrogen atoms, and each yield the same products on combustion. The heat of formation of cellulose and starch are therefore assumed to be equal.

The effect of the functional group on the thermal properties of a molecule has been studied by Kistiakowsky (Ref I) and Springall and Roberts (Ref J). This effect is also evident in the compilations of Kharasch (Ref K), Arthur D. Little (Ref L) and numerous others. All of the above references indicate that the introduction of a functional group (nitro group, amino group, etc) in a molecule will change the heat of combustion and also the heat of formation of that molecule. It is also seen that the change produced is characteristic of the grouping, and is a constant for any particular grouping.

If we therefore represent the starch and cellulose molecules as ROH and R'OH respectively, and these molecules are nitrated to the same degree, the two may be identified as $RONO_2$ and $R'ONO_2$. It has been shown that the heat of formation of ROH and R'OH are equal. The substitution of identical groupings will therefore cause similar variations in the heat of formation of each molecule and the resultant nitrated molecules would have similar heats of formation. The heat of formation of nitrostarch is therefore equal to the heat of formation of nitrocellulose of similar nitrate content. This value is 168.9 kcal/mole, or 617 cal/gm (Ref H).

Using the heats of formation shown in Table VI and the reactions of Tables III and IV, the calculated heat of reaction for the M1A1 Squib is 71.86 cals/squib and for the "Modified" Squib is 58.03 cal/squib.

The experimental heat of reaction was determined for the "Modified" M1A1 Squib Charge since some of the "Modified" T61 Composition was available. The charge of the M1A1 Squib was not available however and the experimental heat of reaction was determined using the complete squib. The method employed is discussed under "Experimental Procedure". The agreement between the experimental and calculated heat of reaction for the M1A1 Squib is quite good 71.86 cals/squib

Discussion of Results (contd)

compared to 73.13 cals/squib. The agreement between the experimental and calculated values for the "Modified" M1A1 Squib is also acceptable, 54.63 cals/squib compared to 58.03 cals/squib, when it is considered that the constituents of the squib charge may vary plus or minus several percent, and that the supplied charge may have come from a different lot from that found in the squib. The experimental values were corrected to constant pressure (as shown on page 70, Ref M).

c. Flam. Temperature:

To estimate the flame temperature, the heat contents (enthalpy) of the products of reaction plus the heat evolved in changes of state were set equal to the heat of reaction, viz

$$-\Delta H_R = \int_{298.16}^{T} \sum_{i=1}^{K} (n_i C_p^{\,i})\,dt + \sum_{i=1}^{K} n_i \Delta H_s^{\,i}$$

where:

ΔH_s is the heat absorbed for a change of state

K is the number of products

n is the number of moles

$C_p^{\,i}$ is the molar heat capacity of the i^{th} product

The heat capacities for all the products are listed in Table VII. Heat capacities for all compounds with the exception of sulfur and potassium chloride are taken from the listings in Glasstone (Ref M).

Values for sulfur and potassium chloride are taken from K. K. Kelley (Refs N and O) respectively. To evaluate the enthalpy change for phase changes the following data, taken from "Selected Values of Thermodynamic Properties" (Ref P) was included:

	Temp	ΔH_s
KCl (c) $\rightarrow$ KCl (g)	1045°K	49.5
KCl (c) $\rightarrow$ KCl (l)	1045°K	6.1
KCl (l) $\rightarrow$ KCl (g)	1680°K	38.8
S (c) $\rightarrow$ S (l)	392°K	0.293
S (l) $\rightarrow$ S (g)	717.7°K	2.5

Discussion of Results (contd)

The values of ΔH_s indicate the heat absorbed in kcal/mole and c, l, and g represents crystal, liquid, and gas phase respectively.

To determine the heat content of a gas between two temperatures it is necessary only to integrate the equations shown in Table VII. For example the heat capacity for n moles of hydrogen is $n(6.50 + .0009T)$. Integrating this equation with respect to temperature we get the enthalpy change

$$\Delta H = \int_{T_o}^{T} (C_p dT), \text{ viz}$$

$$\int_{298.16}^{T} C_p dT = n\left[6.50\,(T-298.16) + \frac{.0009}{2}\,(T^2 - 298.16^2)\right]$$

where:

T is the flame temperature in degrees Kelvin

n is the number of moles of hydrogen

The integrated equations are summed in Appendix II.

Using the procedure shown above, the change in heat content of all the other products can be found as a function of temperature. Summing the heat contents of the individual reaction products gives the total change in enthalpy. This function, ΔH (which is equal to $-\Delta H_R + \Sigma\Delta H_s$) is plotted aginst temperature by assigning various values to T and calculating ΔH. The flame temperature corresponding to the heat of reaction of the squib is obtained directly from Figures I and II. The experimental and calculated flame temperatures of the M1A1 Squib are 1870°K and 1840°K respectively. The experimental and calculated flame temperatures for the "Modified" M1A1 Squib are 2925°K and 3100°K. It is seen therefore that the flame temperature of the "Modified" M1A1 Squib is more than 1000°K greater than the flame temperature of the M1A1 Squib. In Figure I, the value 3.82 is the correction for the heat of vaporization of water and 1.56 is the correction for the heat of fusion of potassium chloride. In Figure II the value .26 is the correction for the heat of vaporization of sulfur, .17 is the correction for the heat of fusion of lead oxide, and 3.56 is the correction for the heat of fusion of potassium chloride.

7. Appraisal of Properties:

In reviewing the results it is seen that the gas volume, which is an indication of the pressure produced by the squibs, is 1.5 times larger for the M1A1 Squib than for the "Modified" M1A1 Squib. At the respective flame temperatures, however, the volume, and consequently the pressure of the gases of both squibs would be approximately the same. The effect of pressure per se on ignition is unknown. Eggert (Ref Q) has shown that nitrogen iodide will detonate

Discussion of Results (contd)

under 300 atmospheres pressure. This is but an isolated case. A gas under pressure will follow a path of least resistance in order to escape. The grade A-5 Black Powder in which the squibs are embedded consists of small grains, and may therefore be described as permeable as there are many channels of escape between these grains. It is safe to assume therefore that the small quantity of gases developed by either squib will escape between the grains of the Black Powder. It is also safe to assume that any grain of black powder is itself quite porous. It is therefore evident that the pressure developed by the gases of both squibs will be quickly dissipated. The pressure would be effective however if minute gas bubbles were occluded in the particles of black powder, and the powder grains formed an impermeable solid mass. The pressure evolved would compress these bubbles adiabatically. The compression would form a hot spot in the black powder and ignition would be effected. The compression of occluded gas bubbles is fully discussed by Bowden and Yoffe (Ref A). For an ideal gas the temperature reached would be derived from the formula $T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{-1/\gamma}$

where T_2 is the final temperature, T_1 the initial temperature, P_2 the final pressure, P_1 the initial pressure, and γ is the ratio of specific heats. Bowden and Yoffe have also shown that the approximate minimum compression ratio must be approximately 20:1 if initial pressure is atmospheric, before ignition can be effected.

It has been shown that the heat of reaction is greater for the M1A1 Squib, than for the "Modified" M1A1 Squib. The heat of reaction by itself has however little significance from the standpoint of ignition. Heat intensity is important. If we combine the heat of reaction with the moles of gas produced we obtain experimental values of 26.05 kcals/mole for the M1A1 Squib compared with 74.01 kcal/mole for the "Modified" M1A1 Squib (Table II). The heat per mole of gas is a better measure of heat concentration than the heat of reaction by itself.

The estimation of the flame temperatures in Figures I and II indicate that the products of the "Modified" M1A1 Squib attain a temperature 1000°K higher than the products of the M1A1 Squib. Tomlinson (Ref F) gives the instantaneous explosion temperature of black powder as 783°K. It is therefore apparent from Figures I and II that either squib can ignite the black powder. The explosion temperature however increases as the time of contact of the black powder with the igniter decreases. It is evident therefore that the much higher flame temperature attained by the products of reaction of the "Modified" M1A1 Squib (2925°K) has a much better chance of igniting the M18 charge of Black Powder, than the products of the M1A1 Squib which reaches a temperature 1000°K less than the "Modified" M1A1 Squib (1870°K).

A further analysis of the reactions shown in Tables III and IV indicates that the only solid residue of the M1A1 Squib is potassium chloride whereas the "Modified" M1A1 Squib yields lead oxide and sulfur as well as potassium chloride. Both lead oxide and sulfur are solids at room temperature. At the flame temperature

Discussion of Results (contd)

it is likely that the solid residues of each squib may be either partially solid, liquid, or gaseous particles. These particles will however revert to solid or perhaps a liquid state on contact with matter at ambient temperature, such as the surrounding powder of the igniter. The total weight of solid matter from the "Modified" M1A1 Squib is .03033 gms compared with .01986 gms for the M1A1 Squib. It is probable that these solids affect the ignition properties of the squibs. A mass in the solid state at any given temperature can concentrate a given amount of heat into a much smaller volume than an equivalent mass in the gaseous state. It is therefore apparent that in this respect the "Modified" M1A1 Squib has a better chance of igniting the M18 Igniter.

The presence of solid residues may be compared to the presence of the grit particles in powders referred to by Bowden and Yoffe (Ref A). These authors have shown that the presence of such particles has a direct influence on the ignition of a powder. It is shown that if these grit particles attain high enough temperatures they will readily initiate an explosion.

The reactions listed in Table IV indicate that one of the products of reaction of the M1A1 Squib is water. No water is formed in the reaction products of the "Modified" M1A1 Squib. It is possible that the water vapor formed in the reaction would condense on contact with the powder to be ignited and might reduce the effectiveness of the M1A1 Squib in igniting that powder.

The individual properties of each squib have been discussed and compared. The cumulative effect of these properties is believed however to be the most important. Thus the heat of reaction in itself is not too significant, but the heat of reaction combined with a knowledge of the physical state and quantity of products is significant. The function of the squib is to ignite a black powder charge (M18 Igniter). There are various means by which ignition may be affected. If it is assumed that ignition takes place by the contact of the hot particles of reaction with the black powder until the black powder reaches its ignition temperature, it is evident that the products of the "Modified" M1A1 Squib, which attain a much higher temperature and consist of a greater quantity of solid particles, can emit more heat in a more concentrated area. The concentration of energy is all important. This is in accord with the work done by Bowden and Yoffe (Ref A).

EXPERIMENTAL PROCEDURE:

8. To determine the gas volume of the individual squib each squib was fired in a 44 ml bomb in one atmosphere of air and the gases formed were measured in an eudiometer. The supply of "Modified" M1A1 Squibs was limited however, and it was therefore necessary to use 15 squibs to obtain an average gas volume determination.

Discussion of Results (contd)

9. In order to analyze the gases formed on firing, nine squibs were fired simultaneously in a 388 ml oxygen bomb. The gases formed were analyzed by means of an Orsat type apparatus, with the exception of sulfur dioxide which was determined by bubbling the gas through .1N iodine solution and titrating the excess iodine with sodium thiosulfate.

10. The heat of reaction of the "Modified" M1A1 charge was determined using one atmosphere of air and generally following the procedure used to determine heat of combustion. An effort was made however to simulate as closely as possible the conditions used in firing the individual squibs, i.e., a loading density of approximately 0.00123 gm/cm^3. The charge from the M1A1 Squib was not available. In order to determine the heat of reaction it was therefore necessary to fire nine squibs simultaneously and to determine the heat capacity of the calorimeter with the squibs. This was accomplished by placing the nine fired squibs in the calorimeter bucket and determining the water equivalent of the calorimeter with benzoic acid.

CONCLUSIONS:

11. Firing tests have shown that the "Modified" M1A1 Squib is a more efficient igniter than the ordinary M1A1 Squib. It is believed that the greater efficiency of the "Modified" M1A1 Squib may be partially explained by the following factors:

a. The greater quantity of solid products formed by the reaction of the "Modified" M1A1 Squib can effect a more intimate and concentrated contact with the igniter. The water vapor formed by the M1A1 Squib may interfere with its ignition efficiency.

b. The flame temperature of the products of reaction of the "Modified" M1A1 Squib is approximately 1000°K higher than that of the M1A1 Squib.

c. Although the heat of reaction of the "Modified" M1A1 Squib is lower than that of the M1A1 Squib, the heat evolved per mole of gas for the former is more than three times the value for the latter.

d. The pressure developed by the products of either squib appears to have a negligible effect on ignition.

12. It is believed that the cumulative effect of these properties is the basis of the greater ignition efficiency of the "Modified" M1A1 Squib.

RECOMMENDATIONS:

13. In view of the fact that many factors may influence ignition it is recommended that a more complete study be made to find out the singular and cumulative effect of each parameter on ignition. This would include a study of

Recommendations (contd)

the effect on ignition of gas volume, flame temperature, heat of reaction and type and quantity of solid and liquid products, as well as other physical properties.

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GLOSSARY OF SYMBOLS:

C_p	=	Molar heat capacity
ΔH	=	Change in Enthalpy = $\int_{T_1}^{T_2} C_p dT$
$(-\Delta H_R)$	=	Heat of Reaction (1 atm pressure, 25°C)
$(-\Delta H_c)$	=	Heat of Combustion (1 atm pressure, 25°C)
$(-\Delta H_f)$	=	Heat of Formation (1 atm pressure, 25°C)
ΔH_s	=	Heat absorbed in going from one state to another
$^\circ K$	=	Degree Kelvin
N	=	Number of samples
n	=	Number of moles of gas
P	=	Pressure
T	=	Flame temperature in degrees Kelvin

11 Inclosures:
1- 2 - Figures I and II
3- 9 - Tables I through VII
10-11 - Appendixes I and II

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FIGURE I

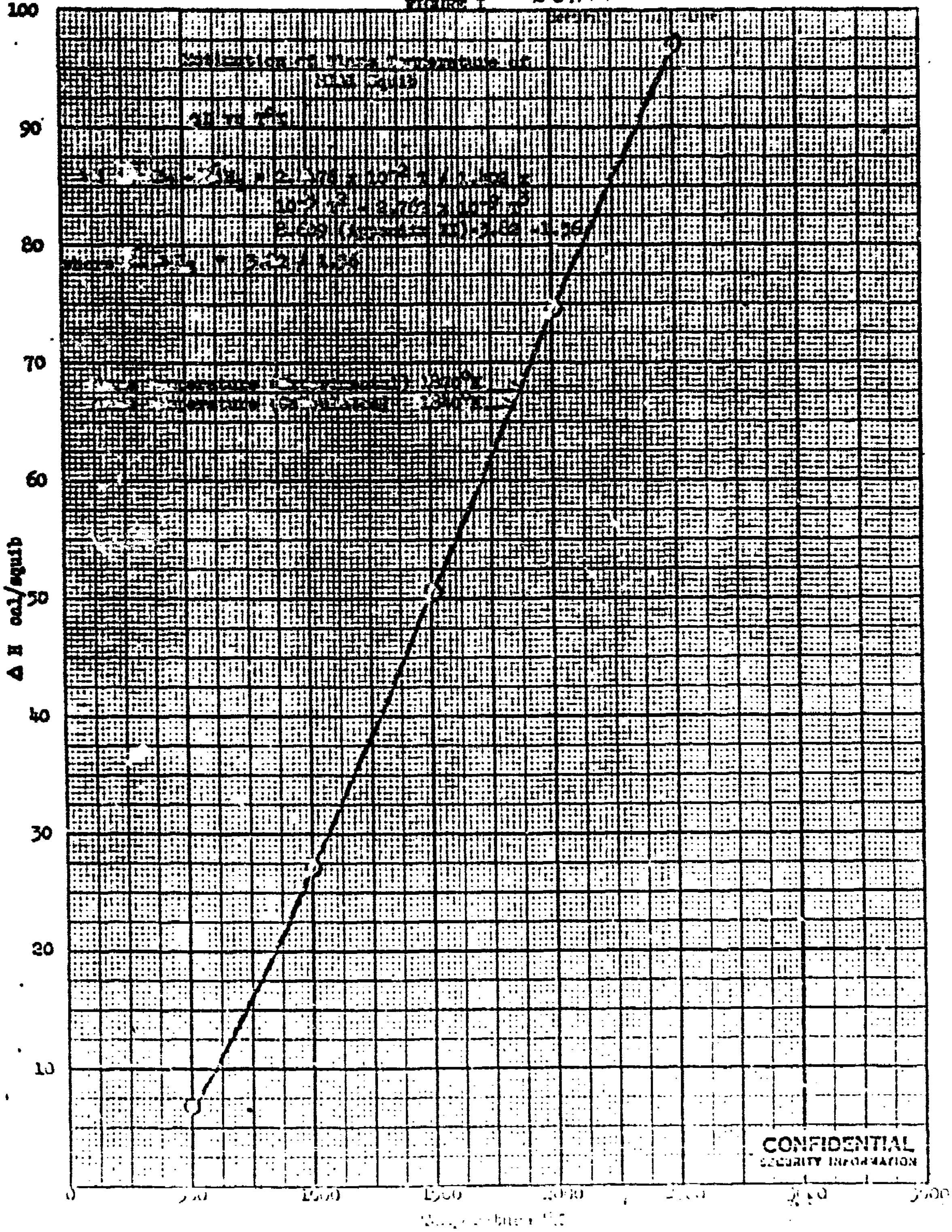

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FIGURE II

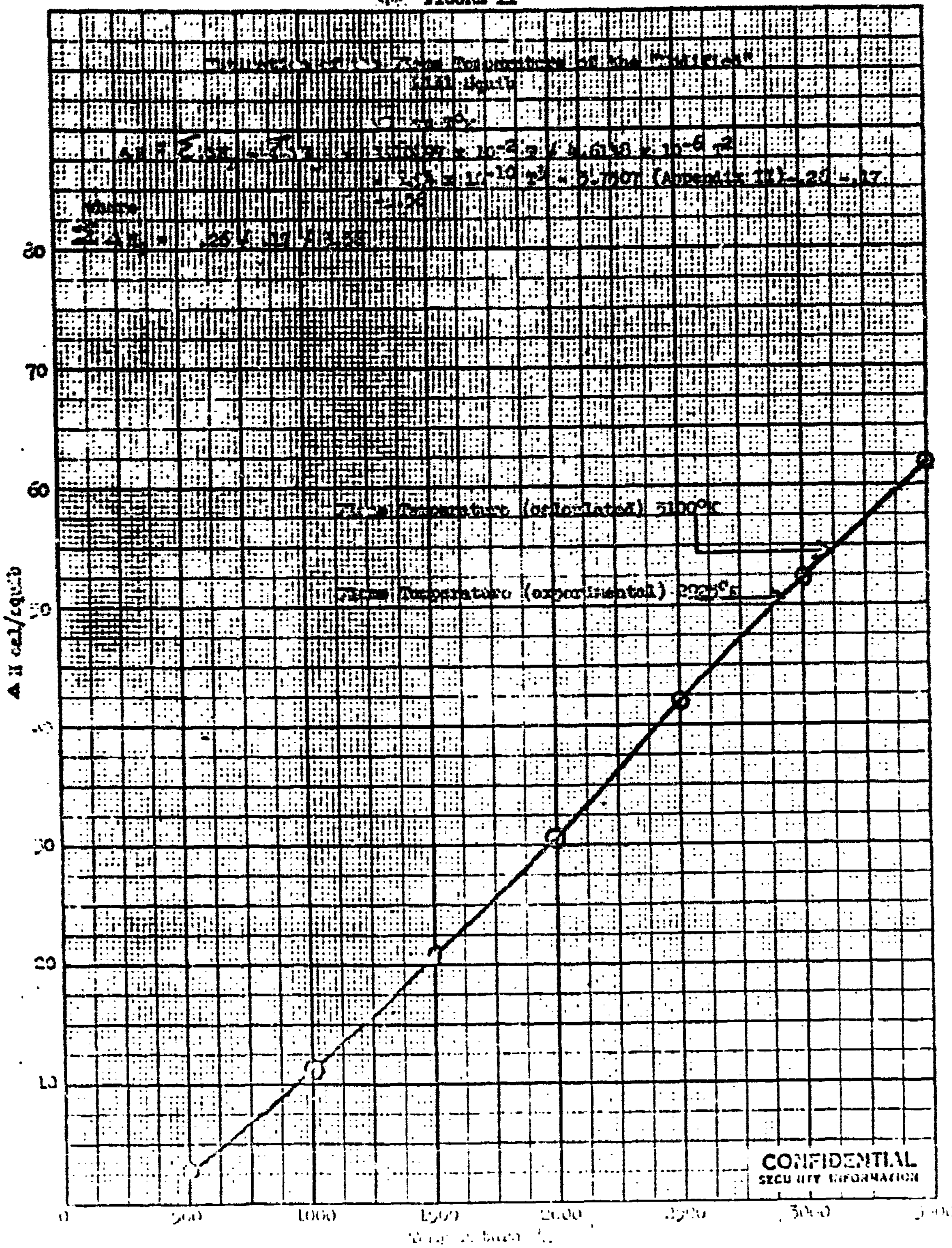
80
70
60
30
20
10
0
500
1000
2000
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TABLE I

Weight (gms) and Gas Volume (ml) of 15 "Modified" M1A1 Squibs

	Weight (grams)	Gas Volume (ml) 0°C-760 mm	Deviation from Average Gas Volume (d)	d^2
	.0510	8.9	.1	.01
	.0578	10.0	1.2	1.44
	.0544	10.0	1.2	1.44
	.0540	10.6	1.8	3.24
	.0531	6.8	2.0	4.00
	.0583	6.5	2.3	5.29
	.0516	8.2	.6	.36
	.0536	10.1	1.3	1.69
	.0565	7.0	1.8	3.24
	.0582	8.5	.3	.09
	.0530	9.5	.7	.49
	.0494	8.6	.2	.04
	.0519	8.0	.8	.64
	.0506	10.0	1.2	1.44
	.0598	10.0	1.2	1.44
Av	.0542	8.8	1.1	$(\Sigma d^2) =$ 24.85

$$\text{Standard deviation of the mean} = \sqrt{\frac{\Sigma d^2}{N(N-1)}} = \sqrt{\frac{24.85}{(14)(15)}} = .33$$

where:

N = No. of samples

TABLE II

Weight (gms) and Gas Volume (ml) of 50 M1A1 Squibs

Weight (grams)	Gas Volume (ml) 0°C and 760 mm	Deviation from Average Gas Volume (d)	d^2
.0519	11.2	1.2	1.44
.0611	13.8	1.4	1.96
.0509	12.1	.3	.09
.0538	12.6	.2	.04
.0526	13.4	1.0	1.0
.0495	12.8	.4	.16
.0515	12.7	.3	.09
.0557	7.5	4.9	24.01
.0445	9.0	3.4	11.56
.0499	11.8	.6	.36
.0516	12.1	.3	.09
.0521	12.5	.1	.01
.0518	12.8	.4	.16
.0581	14.0	1.6	2.56
.0538	13.2	.8	.64
.0512	11.5	.9	.81
.0511	11.9	.5	.25
.0543	12.3	.1	.01
.0632	17.0	4.6	21.16
.0603	12.2	.2	.04
.0543	13.9	1.5	2.25
.0531	13.3	.9	.81
.0532	11.8	.6	.36
.0500	12.4	.0	.0
.0555	14.2	1.8	3.24
.0654	13.5	1.1	1.21
.0484	12.4	.0	.0
.0632	12.3	.1	.01
.0503	12.3	.1	.01
.0504	12.2	.2	.04
.0546	12.7	.3	.09
.0583	12.9	.5	.25
.0473	11.4	1.0	1
.0524	12.3	.1	.01
.0483	10.6	1.8	3.24
.0533	12.6	.2	.04
.0643	15.1	2.7	7.29
.0512	14.4	2.0	4.0
.0515	13.0	.6	.36
.0502	10.9	1.5	2.75
.0530	14.0	1.6	2.56

Table II (contd)

Weight (grams)	Gas Volume (ml) 0°C and 760 mm	Deviation from Average Gas Volume (d)	d^2
.0515	10.8	1.6	2.56
.0557	11.3	1.1	1.21
.0618	10.5	1.9	3.61
.0549	13.6	1.2	1.44
.0464	11.3	1.1	1.21
.0494	12.2	.2	.04
.0495	12.4	.0	0
.0513	12.7	.3	.09
.0547	13.5	1.1	1.21
Av .0524	12.4	1.01	$\Sigma d^2 = 106.83$

$$\text{Standard Deviation of the Mean} = \sqrt{\frac{106.83}{(49)(50)}} = .21$$

TABLE III

Reactions for "Modified" M1A1 Squib

(1)

.01615	.0195		.01346	.00531	.00302	.00169	.00236	.00982
$59KClO_3$ +	$27Pb(CNS)_2$	$\longrightarrow$	$27PbO$ +	$54CO_2$ +	$21SO_2$ +	$27N_2$ +	$33S$	$59KCl$
7,230.45	8,730.99		6,026.67	2,376.54	1,345.26	756.432	[illegible]58.178	4,398.45

(2)

.00062	.00315		.00113	.00072	.00192
$2C$ +	$KClO_3$	$\longrightarrow$	CO_2 +	CO +	KCl
24.02	122.55		44.01	28.01	74.55

(3)

.00455	.00067		.00277	.00245
$2KClO_3$ +	$3C$	$\longrightarrow$	$2\ KCl$ +	$3CO_2$
245.1	36.03		149.1	132.03

(4)

.00351	.00936		.01288
C +	O_2	$\longrightarrow$	CO_2
12.01	32		44.01

$$62KClO_3 + 27Pb(CNS)_2 + 6C + O_2 \longrightarrow 27PbO + 59CO_2 + 21SO_2 + 27N_2 + 33S + 62KCl + CO$$

Note: Numerals above each equation indicate grams of substances taking part in the reaction. Numerals below each equation represent the equivalent weight.

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TABLE IV

Reactions for the M1A1 Squib

(1)	.01630	.01048		.01317	.000896	.00992	.00279
	$8KClO_3$ +	$3C_6H_2(NO_2)_2N_2O$	$\longrightarrow$	$18CO_2$ +	$3H_2O$ +	$8KCl$ +	$6N_2$
	980.4	630.348		792.18	54.048	596.424	168.096
(2)	.00262	.00162		.00233	.00037	.00055	.00098
	$2C_6H_7O_5(NO_2)_3$ +	$3KClO_3$	$\longrightarrow$	$12CO_2$ +	$3N_2$ +	$7H_2O$ +	$3KCl$
	594	367.65		528.12	84.048	126.112	223.659
(3)	.00021	.00109		.000665	.00039	.00025	
	$2C$ +	$KClO_3$	$\longrightarrow$	KCl +	CO_2 +	CO	
	24.02	122.55		74.55	44.01	28.01	
(4)	.01243	.00183		.006696	.00756		
	$2KClO_3$ +	$3C$	$\longrightarrow$	$3CO_2$	+ $2KCl$		
	245.1	36.03		132.03	149.1		
(5)	.00071	.00008		.00063			
	$2H_2O$ $\longrightarrow$	$2H_2$ +		O_2			
	36.032	4.032		32			
(6)	.00202	.00539		.00741			
	C +	O_2	$\longrightarrow$	CO_2			
	12.01	32		44.01			

$$14KClO_3 + 3C_6H_2(NO_2)_2N_2O + 2C_6H_7O_5(NO_2)_3 + 6C \longrightarrow 35CO_2 + 8H_2O + 14KCl + 9N_2 + CO + 2H_2$$

Note: Numerals above each equation indicate grams of substance taking part in the reaction. Numerals below each equation represent the equivalent weight.

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TABLE V

Analysis of Gaseous Products

Gases	M1A1 Squib		"Modified" M1A1 Squib	
	% by Volume	Moles per Squib	% by Volume	Moles per Squib
CO_2	27.1	6.8×10^{-4}	21.0	5.0×10^{-4}
CO	.4	1.3×10^{-5}	1.1	2.7×10^{-5}
SO_2	—	—	.34	8.9×10^{-6}
H_2	1.6	4.0×10^{-5}	—	—
O_2 and N_2	Remainder	—	Remainder	—

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TABLE VI

Heats of Formation $(-\Delta H_f)$

Substance	Heat of Formation, kcal/mole at 25°C	Reference
$Pb(CNS)_2$	-30.7	E
$KClO_3$	91.33	E
CO_2	94.45	E
CO	26.84	E
$H_2O(l)$	68.37	E
$H_2O(g)$	57.80	E
KCl	104.361	E
$C_6H_2N_4O_5$	-43.	This Report
$C_6H_7O_{11}N_3$	183.0	This Report

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TABLE VII

Equations for the Heat Capacity of the Products of Reaction

Substance	Heat Capacity, cals/mole-deg	Reference
CO_2	$6.396 + 10.1 \times 10^{-3} T - 3.405 \times 10^{-6} T^2$	M
CO	$6.342 + 1.836 \times 10^{-3} T - 2.801 \times 10^{-7} T^2$	M
N_2	$6.449 + 1.413 \times 10^{-3} T - .0807 \times 10^{-6} T^2$	M
SO_2	Same as CO_2	M
H_2O	$7.219 + 2.374 \times 10^{-3} T + .267 \times 10^{-6} T^2$	M
KCl	$10.93 + 3.76 \times 10^{-3} T$	O
S	(monoclinic) $3.56 + 6.95 \times 10^{-3} T$; (gas) $7.75 + .888 \times 10^{-3} T$	M
PbO	$10.33 + 3.18 \times 10^{-3} T$	M
N_2	$6.50 + .0009T$	M
C	$2.673 + .617 \times 10^{-3} T + .1169 \times 10^{-6} T^2$	M

APPENDIX I

Calculation of the Heat of Reaction ($-\Delta H_r$)

"Modified" M1A1 Squib (Equations correspond to Reactions of Table III)

(1) $59\ (91.33) + 27\ (-30.7) \rightarrow 27\ (52.46) + 54\ (94.45) + 21\ (70.92) + 59\ (104.361)$

$$9{,}603.77 \times \frac{.0195}{8730.99} \times 1000 = 21.449 \text{ cals}$$

(2) $91.33 \rightarrow 94.45 + 26.84 + 104.361$

$$134.32 \times \frac{.00315}{122.55} \times 1000 = 3.45$$

(3) $2\ (91.33) \longrightarrow 2(104.361) + (94.45)$

$$296.381 \times \frac{.00455}{245.1} \times 1000 = 5.50$$

(4) $0 \longrightarrow 94.45$

$$94.45 \times \frac{.00936}{32} \times 1000 = 27.63$$

$$-\sum \Delta H_r = 58.029 \text{ cals/squib}$$

M1A1 Squib (Equations correspond to Reactions of Table IV)

(1) $8\ (91.33) + 3\ (43) \rightarrow 18\ (94.45) + 3\ (68.37) + 8\ (104.361)$

$$2140.4 \times 1000 \times \frac{.01048}{[illegible]} = 35.59$$

(2) $2\ (168.9) + 3\ (91.33) \rightarrow 12\ (94.45) + 7\ (68.37) + 3\ (104.361)$

$$1313.28 \times 1000 \times \frac{.00262}{594} = 5.79$$

<u>Appendix I</u> (contd)
<u>MiAl Squib</u> (contd)

(3) $(91.33) \rightarrow (104.361) + (94.45) + (26.84)$ $\qquad 134.321 \times \frac{.00109}{122.55} = 1.19$

(4) $2\ (91.33) \rightarrow 3\ (94.45) + 2\ (104.361)$

$$309.412 \times 1000 \times \frac{.01243}{245.1} = 15.69$$

(5) $2\ (57.801) \rightarrow 0$

$$-\ (115.602) \times 1000 \times \frac{.00071}{36.032} = -2.28$$

(6) $0 \rightarrow (94.45)$

$$94.45 \times 1000 \times \frac{.00202}{12.01} = 15.88$$

$$-\sum \Delta H_r = 71.86 \text{ cals/squib}$$

APPENDIX II

Integrated Heat Capacity Equations
(based on moles of product per mole of reactant)

"Modified" M1A1 Squib

$$
\begin{aligned}
CO_2 &= .003936T + .000003108T^2 - .000000000698T^3 - 1.468 \\
HCl &= .004254T + .0000007312T^2 - 1.33 \\
CO &= .000163T + .0000000236T^2 - .0000000000024T^3 - .0508 \\
SO_2 &= .000234T + .000000185T^2 - .000000000042T^3 - .0875 \\
S &= .0006967T + .0000000399T^2 - .229 \\
FeO &= .000623T + .000000096T^2 - .1942 \\
N_2 &= .000389T + .0000000426T^2 - .0000000000016T^3 - .1197 \\
C &= .000794T + .000000388T^2 + .00000000001157T^3 - .2715 \\
\int_T \sum C_p dT &= .0110897T + .0000046148T^2 - .0000000000694T^3 - 3.7507
\end{aligned}
$$

M1A1 Squib

$$
\begin{aligned}
CO_2 &= .01562T + .00001233T^2 - .000000002773T^3 - 5.829 \\
H_2O &= .0005892T + .000000968T^2 + .0000000000073T^3 - .18 \\
HCl &= .005607T + .0000009644T^2 - 1.758 \\
N_2 &= .0014122T + .0000001547T^2 - .00000000000589T^3 - .43 \\
CO &= .0000565T + .00000000819T^2 - .0176 \\
H_2 &= .00025794T + .00000001785T^2 - .0785 \\
O_2 &= .00006095T + .0000000168T^2 - .00000000000339T^3 - .019 \\
C &= .0008679T + .000000425T^2 + .00000000001265T^3 - .2969 \\
\int_T \sum C_p dT &= .024476T + .0000142T^2 - .000000027623 - 8.609
\end{aligned}
$$